SHORT STRUCTURAL PAPERS

The Structures of Thallium Cadmium Triiodide and Dirubidium Iron Tetraiodide

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Abstract. TlCdI$_3$, orthorhombic, *Pnma*, $a = 10 \cdot 080$ (2), $b = 4 \cdot 412$ (1), $c = 16 \cdot 289$ (3) Å, $Z = 4$, $V = 724 \cdot 4$ (2) Å^3, $D_c = 6 \cdot 39$ Mg m^{-3}. The NH$_4$CdCl$_3$-type structure is adopted. Rb$_2$FeI$_4$, monoclinic, *P*2$_1$, $a = 7 \cdot 705$ (2), $b = 8 \cdot 182$ (2), $c = 10 \cdot 341$ (2) Å, $\beta = 109 \cdot 87$ (2)°, $Z = 2$, $V = 613 \cdot 1$ (2) Å^3, $D_c = 3 \cdot 98$ Mg m^{-3}. The Sr$_2$GeS$_4$-type structure is adopted.

Introduction. The investigations of the title compounds form part of the studies of compounds in the system AI–BI_2, A representing an alkali metal, In or Tl and B a first-row transition metal, Zn, Cd, Hg or Pb.

The phase diagram of the system TlI–CdI$_2$ was constructed by Il-yasov & Bergman (1959) and Il-yasov, Dionisev & Bergman (1962). Recently the structure of Rb$_2$CoI$_4$ (Seifert & Stäudel, 1977), which is isostructural with Rb$_2$FeI$_4$, was reported. Also Cs$_2$HgI$_4$ (Pakhomov & Fedorov, 1973) is isostructural with Rb$_2$FeI$_4$ {[101] in the reported Cs$_2$HgI$_4$ structure is the same as [001] in Rb$_2$FeI$_4$}.

Single crystals were grown using the Bridgman method. The crystals of TlCdI$_3$ have one preferred growing direction, parallel to the *b* axis, giving needle-shaped crystals. With Rb$_2$FeI$_4$ no preferred growing direction was noticed. Crystal symmetry and approximate cell parameters of both compounds were determined from zero- and upper-level Weissenberg photographs. The systematic absences (0*k*0 with $k = 2n + 1$ for Rb$_2$FeI$_4$ and 0*kl* with $k + l = 2n + 1$ and *hk*0 with $k = 2n + 1$ for TlCdI$_3$) suggest the space groups *Pnma* or *Pn*2$_1$*a* for TlCdI$_3$ and *P*2$_1$ or *P*2$_1$/*m* for Rb$_2$FeI$_4$.

A crystal of TlCdI$_3$ of dimensions 0·02–0·03 mm was mounted along [010] and a crystal of Rb$_2$FeI$_4$ of dimensions 0·15–0·20 mm along [011] on an Enraf–Nonius three-circle diffractometer. Graphite-monochromatized Mo *K*α radiation ($\lambda = 0 \cdot 71069$ Å; $\mu = 18 \cdot 8$ mm^{-1} for Rb$_2$FeI$_4$ and $37 \cdot 8$ mm^{-1} for TlCdI$_3$) was used for the data collection. The ω-scan technique was employed with θ ranges of 4–25° for Rb$_2$FeI$_4$, and 3–

25° for TlCdI$_3$, and a scan width of $(1 \cdot 9 + \tan \theta)°$ for both compounds. 2145 (Rb$_2$FeI$_4$) and 2129 (TlCdI$_3$) reflexions were measured. Of the independent reflexions, 1195 and 583 were significant (358 and 117 insignificant) for Rb$_2$FeI$_4$ and TlCdI$_3$ respectively. A correction for absorption was made with a program developed by de Graaff (1973). After correction for Lorentz and polarization effects, the intensities were reduced to F_o values and symmetry-related reflexions were averaged. All crystallographic calculations were carried out on the Leiden University IBM 370/158 computer using a set of computer programs written or modified by Rutten-Keulemans & de Graaff (private communication). Scattering factors taken from Cromer & Waber (1968) were used with corrections for the real and imaginary part of the anomalous dispersion. The function minimized during the least-squares refinement was $w_F(F_o - F_c)^2$, using the weighting scheme $w_F = 1/\sigma_F^2$.

The refinement was started with the positions of NH$_4$CdCl$_3$ (Brasseur & Pauling, 1938) as a model. Full-matrix refinement in *Pnma* of positional parameters and anisotropic thermal parameters for all ions led to convergence at $R_F = (F_o - F_c)/F_o = 4 \cdot 74$ and $R_{wF} = [w_F(F_o - F_c)^2/w_F F_o^2]^{1/2} = 4 \cdot 44$. Extinction correction resulted in $R_F = 3 \cdot 65$ and $R_{wF} = 3 \cdot 53$.

Starting with the positions found for *Pnma* full-matrix refinement of positional parameters and anisotropic thermal parameters for all ions (with extinction correction) in space group *Pn*2$_1$*a* led to convergence at $R_F = 3 \cdot 41$ and $R_{wF} = 3 \cdot 24$. The differences between the x and z parameters of both refinements are less than the standard deviations. The y parameters of both refinements are given in Table 1 together with the x and z parameters resulting from the refinement in *Pnma*.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34273 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Although the lowering of the symmetry is significant according to the R_F ratio test we believe the space group to be *Pnma*. The reasons for believing this are: (1) the U_{22} parameters in the refinement in *Pnma* give no reason to expect a deviation in the [010] direction, (2) the shifts of the ions in the refinement in *Pn2₁a* are random and (3) the largest deviation in the [001] direction is only 0·03 Å.

Measurements with second-harmonic generation (Kurtz & Perry, 1968), to establish whether or not the compound is centrosymmetric, did not yield a reliable result. There were a considerable number of spurious signals making it very difficult to determine whether or not a second harmonic signal is present. The interatomic bond distances and angles are listed in Tables 2 and 3.

For the refinement of Rb_2FeI_4 we took the positions of Sr_2GeS_4 as starting parameters because the axis ratio and the systematically absent reflexions are the same for both compounds (Philippot, Ribes & Maurin, 1971) and because the distances calculated from a three-dimensional Patterson map agree with this structure. Full-matrix refinement of positional and isotropic thermal parameters in space group $P2_1/m$ led to convergence at $R_F = \sum (|F_o| - |F_c|)/\sum |F_o| = 4·81$ and $R_{wF} = [\sum w_F(|F_o| - |F_c|)^2/\sum w_F F_o^2]^{1/2} = 5·52$, w_F being $1/\sigma_F^2$. The refinement in $P2_1$ converges at $R_F = 4·39$ and $R_{wF} = 5·03$. Because of the ratio of the R values of the refinements in $P2_1/m$ and $P2_1$ and the significance of the shifts of the ions in $P2_1$ with respect to $P2_1/m$ we have concluded that the space group must be $P2_1$. Measurements with second-harmonic generation did not yield a reliable result as the sample was sensitive to the laser beam. It was therefore not possible to determine whether the measured signal was a second harmonic or a spurious signal. Extinction correction led to $R_F = 4·07$ and $R_{wF} = 4·45$. We could not decide between the above structure and the inverted one as both give the same R values. The results of the refinement are given in Table 4. In Table 5 some distances and bond angles are given.

Table 1. *Positional parameters of the refinement in space group Pnma and the y parameter of the refinement in Pn2₁a for TlCdI₃*

	x	y	z	y(Pn2₁a)
Tl	0·43617 (10)	0·25	−0·17606 (6)	0·25
Cd	0·16776 (15)	0·25	0·05634 (9)	0·2435 (12)
I(1)	0·16350 (12)	0·25	0·48989 (8)	0·2508 (12)
I(2)	0·29119 (11)	0·25	0·21392 (7)	0·2481 (14)
I(3)	0·02409 (12)	0·25	−0·10698 (7)	0·2453 (10)

Table 2. *Interatomic distances (Å) for TlCdI₃*

Tl–I(1)	3·800 (2)	I(1)–I(1)	4·415 (1)
Tl–I(1)	3·631 (2) ×2	I(1)–I(1)	3·980 (3)
Tl–I(2)	3·578 (2) ×2	I(1)–I(2)	4·288 (3)
Tl–I(2)	3·651 (2) ×2	I(1)–I(3)	4·103 (3)
Tl–I(3)	3·642 (2)	I(1)–I(3)	4·156 (3)
Tl–I(3)	4·302 (2)	I(2)–I(2)	4·415 (1)
Cd–I(1)	2·989 (2) ×2	I(2)–I(3)	4·243 (3)
Cd–I(2)	2·851 (3)	I(2)–I(3)	4·104 (2)
Cd–I(3)	3·028 (2)	I(3)–I(3)	4·415 (1)
Cd–I(3)	3·048 (2) ×2	I(3)–I(3)	4·153 (3)

Table 4. *Positional parameters for Rb₂FeI₄*

	x	y	z
Rb(1)	0·1971 (2)	0·7408 (7)	0·0383 (1)
Rb(2)	0·2917 (2)	0·7391 (6)	0·5825 (1)
Fe	0·2057 (2)	0·2444 (7)	0·7878 (2)
I(1)	0·4208 (1)	0·2485 (7)	0·6390 (1)
I(2)	0·3741 (2)	0·2500	0·0569 (1)
I(3)	−0·0167 (5)	0·0107 (4)	0·7342 (3)
I(4)	0·0199 (5)	0·0034 (4)	−0·7252 (3)

Table 3. *Bond angles (°) and their estimated standard deviations for TlCdI₃*

I(1)–Tl–I(1)	64·73 (3)	I(2)–Tl–I(3)	69·27 (3)
I(1)–Tl–I(2)	71·00 (3)	I(2)–Tl–I(3)	74·40 (3)
I(1)–Tl–I(2)	140·33 (2)	I(2)–Tl–I(3)	61·48 (3)
I(1)–Tl–I(3)	111·93 (3)	I(2)–Tl–I(3)	71·14 (3)
I(1)–Tl–I(3)	128·84 (4)	I(3)–Tl–I(3)	119·24 (3)
I(1)–Tl–I(1)	88·02 (2)	I(1)–Cd–I(1)	95·21 (5)
I(2)–Tl–I(2)	135·71 (4)	I(1)–Cd–I(2)	94·45 (5)
I(1)–Tl–I(2)	79·86 (3)	I(1)–Cd–I(3)	87·37 (4)
I(1)–Tl–I(2)	124·00 (4)	I(1)–Cd–I(3)	85·63 (2)
I(1)–Tl–I(2)	62·51 (3)	I(1)–Cd–I(3)	173·50 (6)
I(1)–Tl–I(3)	142·10 (2)	I(2)–Cd–I(3)	177·30 (7)
I(2)–Tl–I(2)	76·20 (3)	I(2)–Cd–I(3)	91·91 (4)
I(2)–Tl–I(2)	91·39 (1)	I(3)–Cd–I(3)	86·23 (4)
I(2)–Tl–I(2)	140·39 (3)	I(3)–Cd–I(3)	92·81 (5)
I(2)–Tl–I(3)	141·83 (2)		

Table 5. *Distances (Å) and some bond angles (°) for Rb₂FeI₄*

Rb(1)–I(1)	3·644 (1)	Rb(2)–I(1)	3·689 (2)
Rb(1)–I(2)	3·795 (2)	Rb(2)–I(2)	3·744 (2)
Rb(1)–I(3)	3·675 (5)	Rb(2)–I(3)	3·788 (5)
Rb(1)–I(3)	3·809 (5)	Rb(2)–I(3)	3·763 (4)
Rb(1)–I(4)	3·760 (5)	Rb(2)–I(4)	3·797 (4)
Rb(1)–I(4)	3·710 (4)	Rb(2)–I(4)	3·779 (5)
Rb(1)–I(2)	4·280 (6)	Rb(2)–I(1)	4·129 (7)
Rb(1)–I(2)	4·337 (6)	Rb(2)–I(1)	4·279 (7)
Fe–I(1)	2·618 (2)		
Fe–I(2)	2·640 (2)	I–I	4·03–4·84
Fe–I(3)	2·638 (6)		
Fe I(4)	2·634 (6)		
I(1)–Fe–I(2)	115·9 (1)	I(2)–Fe–I(3)	108·7 (2)
I(1)–Fe–I(3)	110·6 (2)	I(2)–Fe–I(4)	107·1 (2)
I(1)–Fe–I(4)	110·0 (2)	I(3)–Fe–I(4)	103·9 (1)

Discussion. $TlCdI_3$ consists of double chains of edge-sharing CdI_6 octahedra with Tl^+ ions between the double chains in nine coordination. Haupt, Huber & Preut (1974) have given a more detailed description of $RbPbI_3$, which is isostructural with $TlCdI_3$. The ABI_3 compounds with the NH_4CdCl_3-type structure are listed in Table 6. Although Rb^+ has almost the same

Table 6. *Cell parameters of several ABI_3 compounds*

ND = neutron diffraction; XD = X-ray diffraction.

Compound	Type of diffraction	a (Å)	b (Å)	c (Å)
$TlMnI_3$	ND	10·070 (1)	4·2963 (4)	16·171 (2)
$TlFeI_3$	ND	9·967 (1)	4·2407 (3)	15·981 (1)
$TlCdI_3$	XD	10·080 (2)	4·412 (1)	16·289 (3)
$KPbI_3$	XD	10·169 (2)	4·716 (1)	17·359 (4)
$RbPbI_3^b$	XD	10·274 (1)	4·773 (1)	17·381 (2)
$CsPbI_3^a$	XD	10·46	4·797	17·78

References: (*a*) Moller (1959); (*b*) Haupt, Huber & Preut (1974).

Table 7. *Cell parameters of ternary iodides with the Sr_2GeS_4 structure*

	a (Å)	b (Å)	c (Å)	β (°)
K_2MnI_4	7·943 (4)	8·197 (3)	9·525 (2)	108·36 (5)
$K_2MnI_4^a$	7·922	8·229	9·719	108·3
Rb_2MnI_4	7·844 (2)	8·253 (2)	10·281 (1)	109·45 (1)
$Rb_2MnI_4^a$	7·854	8·264	10·304	109·4
K_2FeI_4	7·832 (3)	8·161 (3)	9·663 (2)	108·42 (4)
Rb_2FeI_4	7·705 (2)	8·182 (2)	10·341 (2)	109·87 (2)
K_2CoI_4	7·723 (5)	8·087 (4)	9·688 (2)	108·56 (6)
$K_2CoI_4^b$	7·702	8·090	9·677	108·4
Rb_2CoI_4	7·630 (3)	8·143 (3)	10·382 (2)	109·56 (6)
$Rb_2CoI_4^b$	7·657	8·144	10·384	109·8
Tl_2CoI_4	7·521 (3)	7·972 (3)	9·755 (2)	109·28 (6)
$Tl_2CoI_4^b$	7·519	7·972	9·762	108·9
K_2ZnI_4	7·745 (3)	8·121 (2)	9·665 (1)	108·28 (6)
Rb_2ZnI_4	7·642 (2)	8·176 (2)	10·371 (3)	109·84 (2)
In_2ZnI_4	7·471 (3)	7·967 (3)	9·827 (2)	109·57 (4)
Tl_2ZnI_4	7·548 (2)	7·997 (2)	9·730 (1)	109·00 (5)
Rb_2CdI_4	8·004 (7)	8·323 (3)	10·164 (8)	108·96 (7)
Cs_2CdI_4	7·799 (4)	8·381 (2)	11·019 (3)	110·77 (3)
Cs_2HgI_4	7·722 (3)	8·376 (3)	11·040 (5)	110·47 (5)
$Cs_2HgI_4^c$	7·94	8·46	11·32	110·66

References: (*a*) Seifert & Kischka (1978); (*b*) Seifert & Stäudel (1977); (*c*) Pakhomov & Federov (1973), transformed.

radius as Tl^+ compounds $RbBI_3$ do not have the NH_4CdCl_3 structure, except for $RbPbI_3$. Perhaps the occurrence of compounds having the NH_4CdCl_3 structure is favoured by the lone pair of Tl^+ which fits into the structure rather well because one of the Tl^+-I^- distances is considerably larger than the rest (see Table 2).

Rb_2FeI_4 consists of isolated FeI_4^{2-} tetrahedra with the Rb^+ ion in 6 + 2 coordination. It has rows of $I(3)$ and $I(4)$ ions along the b axis determining the length of the b axis. One would expect therefore that the Rb, $I(1)$ and $I(2)$ ions have too much space in the [010] direction. That this is actually the case can be seen from the anisotropic parameters. If one were to rotate the tetrahedra in order to reduce the space for Rb, $I(1)$ and $I(2)$, the coordination of the Rb ions would be lowered. Probably because of this change in coordination, Rb_2FeI_4 has a non-modified Sr_2GeS_4-type structure. Some compounds isostructural with Rb_2FeI_4 are listed in Table 7.

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